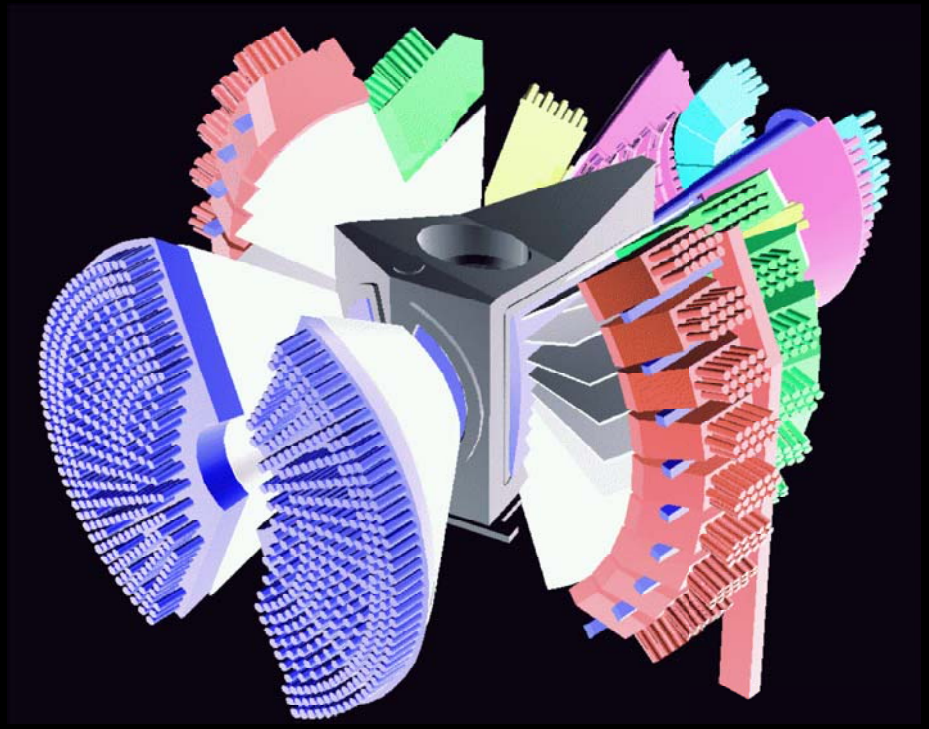
Time-Resolved, *In-Situ* Neutron Diffraction Studies of Hydrothermal Reactions



ACNS, Knoxville, TN - June 24th 2002

Dermot O'Hare,
Inorganic Chemistry Laboratory
University of Oxford, UK

Solid State Reactions that we have Investigated using Time-Resolved *In Situ* Powder Diffraction

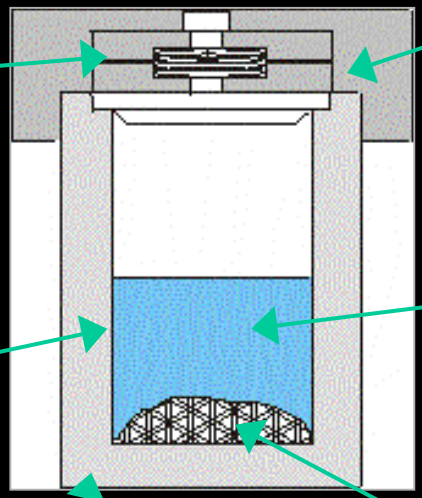
Synchrotron X-Ray Experiments

- Crystallisation from Solution
- Intercalation Reactions
- Hydrothermal Reactions
- Sol-Gel Syntheses
- Solid State Syntheses in Molten-Salt Fluxes
- Classical Solid Phase Reactions

Neutron Experiments

- Hydrothermal Reactions

Hydrothermal Synthesis



Many experimental variables:

- starting mixture composition
- choice of reagents
- temperature
- time
- % fill of reaction vessel

Sealed reaction vessel

- observation of reaction course is difficult

It remains very difficult (impossible) to predict the outcome of new reactions.

$\Rightarrow$ need to develop methods for *in-situ* study

Key Features of Energy Dispersive X-ray Powder Diffraction using Synchrotron Radiation

Advantages

- Very fast data collection times; typically (1 – 30 sec)
- High energy incident X-ray photon beam; give excellent penetration through cell materials
- Large volume cells; allows us to reproduce laboratory scale syntheses

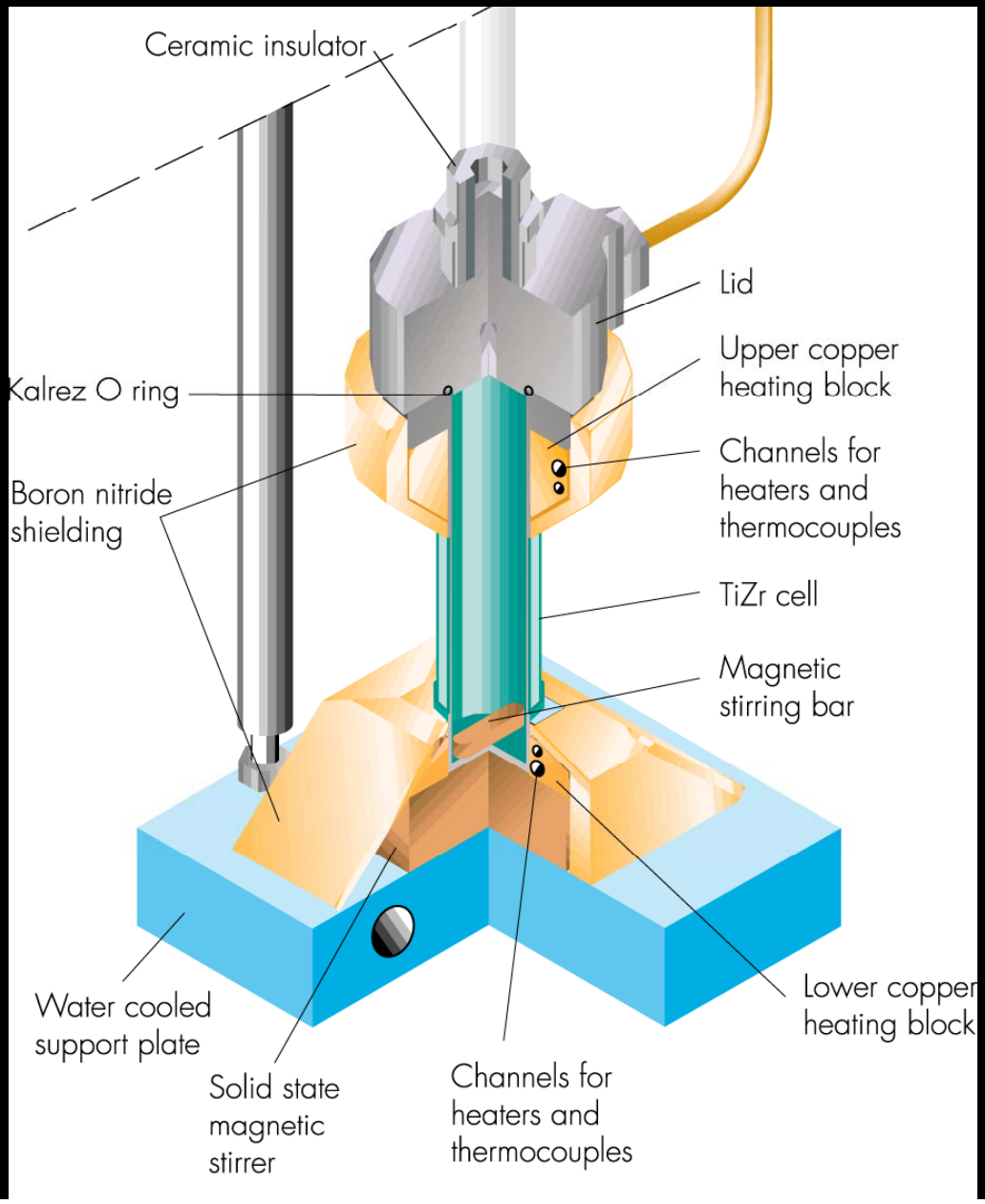
Disadvantages

- Incident beam profile not well characterised
- Poor resolution, especially for high d-spacings
- Structure solution and/or refinement impossible
- Strongly absorbing samples

Time-Resolved *In-Situ* Powder Neutron Diffraction

- **Cell Design**
- **Gem Diffractometer**
- **Hydrothermal Chemistry**
  - Synthesis of Zeolites
  - Synthesis of *t*-$BaTiO_3$

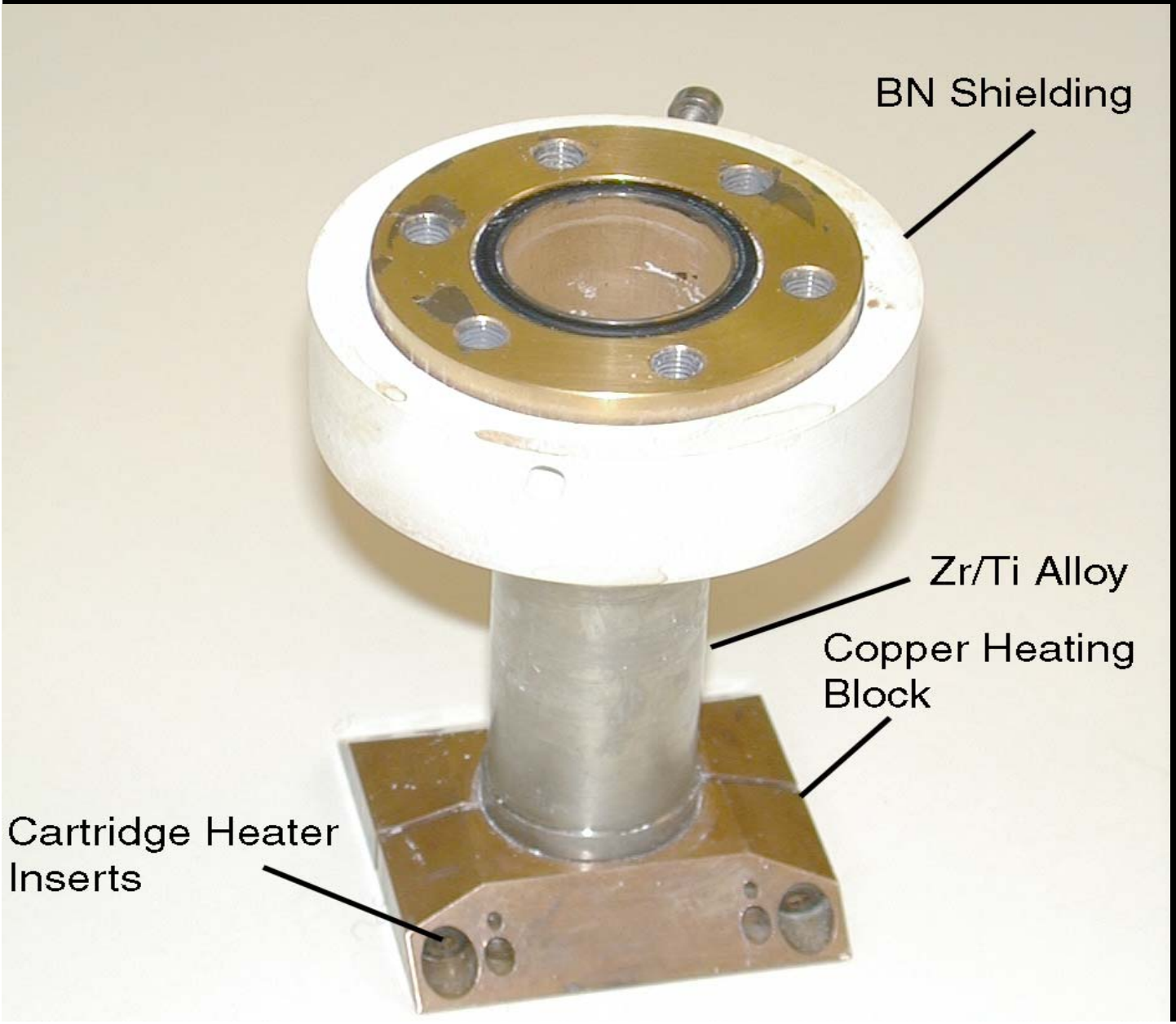
Schematic Diagram of the Oxford/Isis Hydrothermal Cell



- Constructed from null-scattering Ti-Zr alloy
- 25 mL volume
- 4 cm high window of material exposed to beam
- Internal surfaces sputtered with gold

Walton *et al. Rev. Sci. Instrum.* **70** (1999) 3391

Photograph of the Oxford/ISIS Hydrothermal Cell



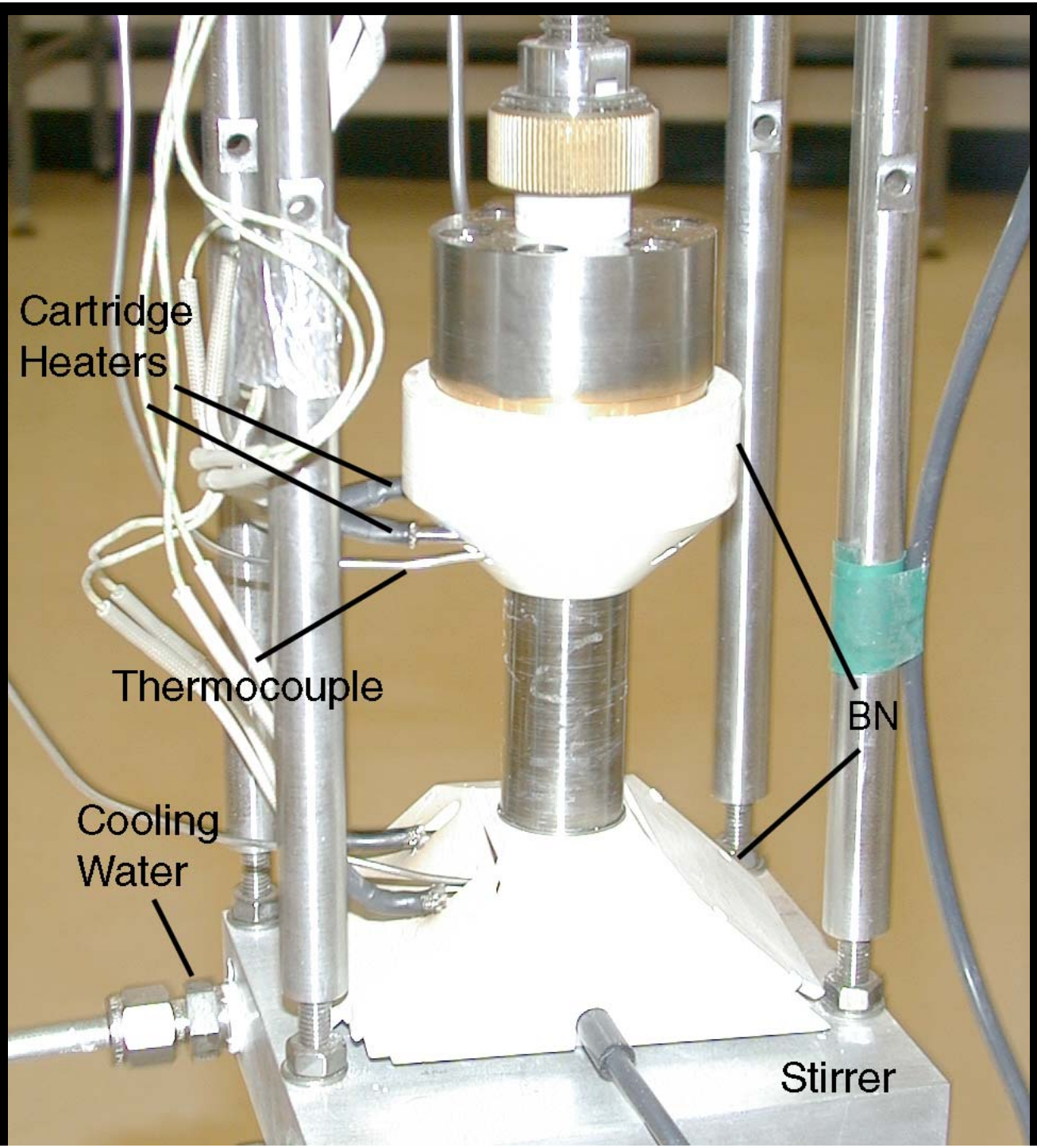
Hydrothermal Reaction Cell

- constructed from null-scattering Ti-Zr alloy

- 25 mL volume

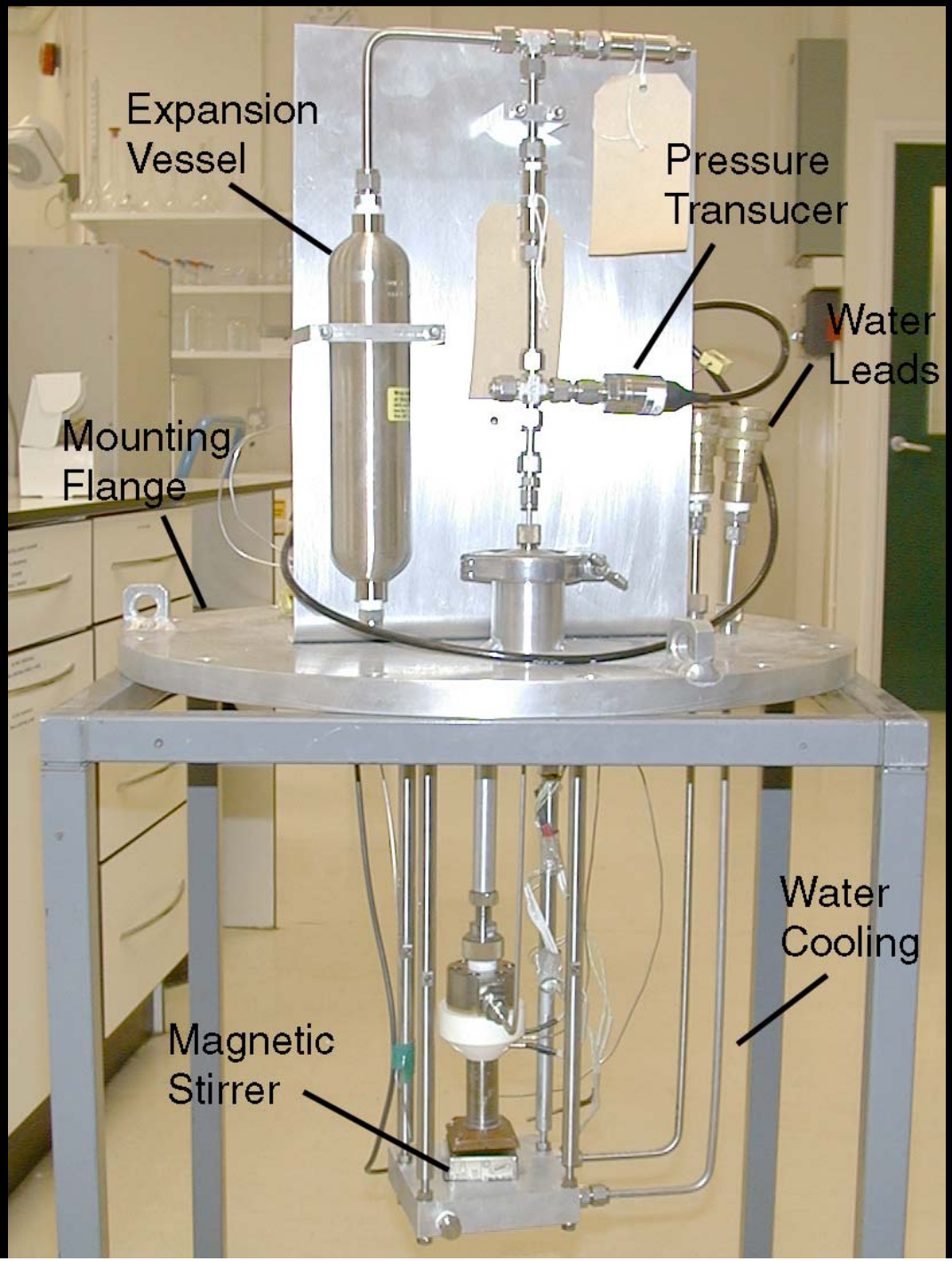
- 4 cm high window of material exposed to beam

- Internal walls sputtered with 100μm of gold



Close-up Photograph of the Assembled Hydrothermal Cell

- Null Scattering Alloy
- Copper Heating Blocks require BN Shielding
- Facility for stirring reactions



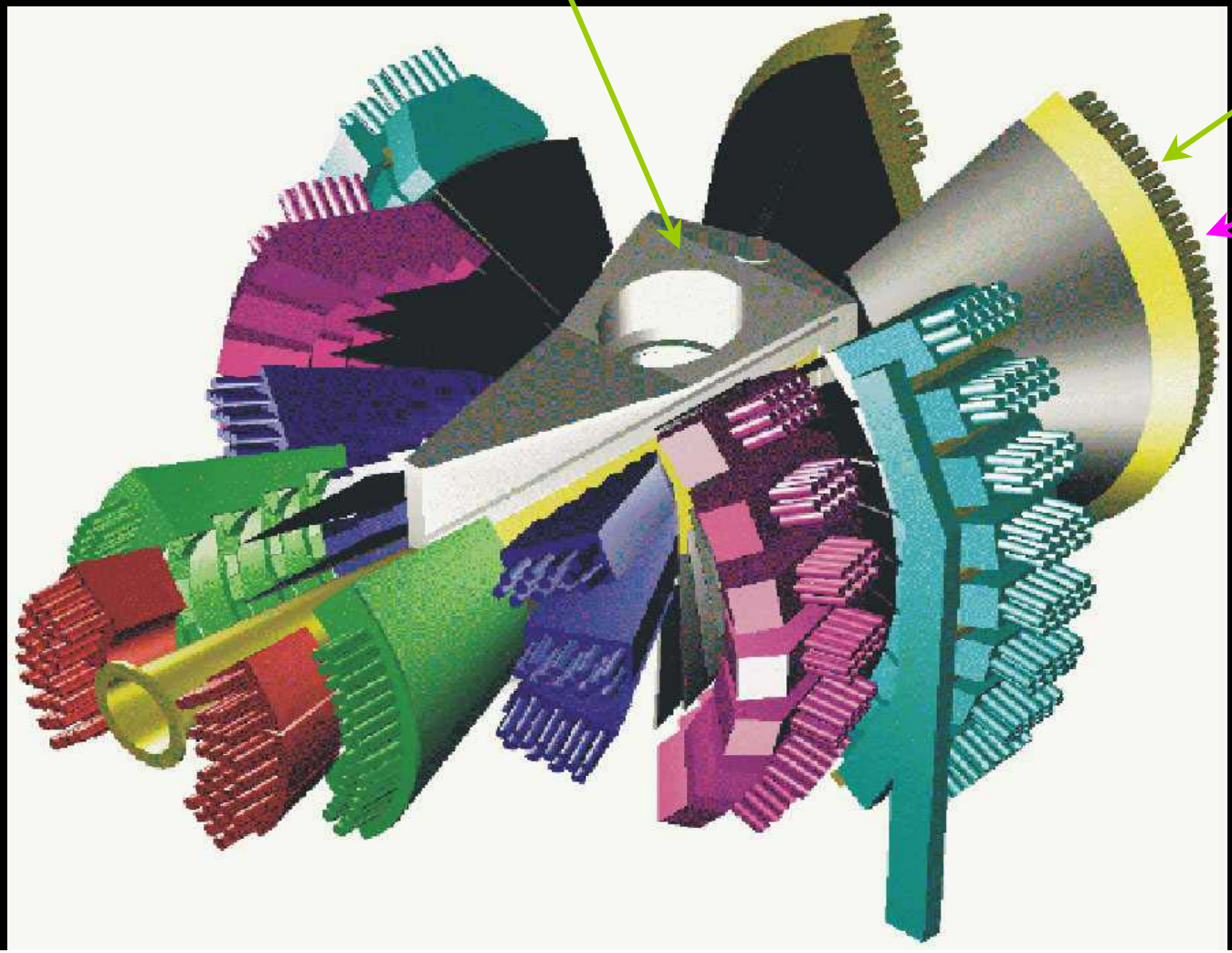
Photograph of the Fully Assembled Hydrothermal Cell

GEM: Shining Bright

Instrument Parameters

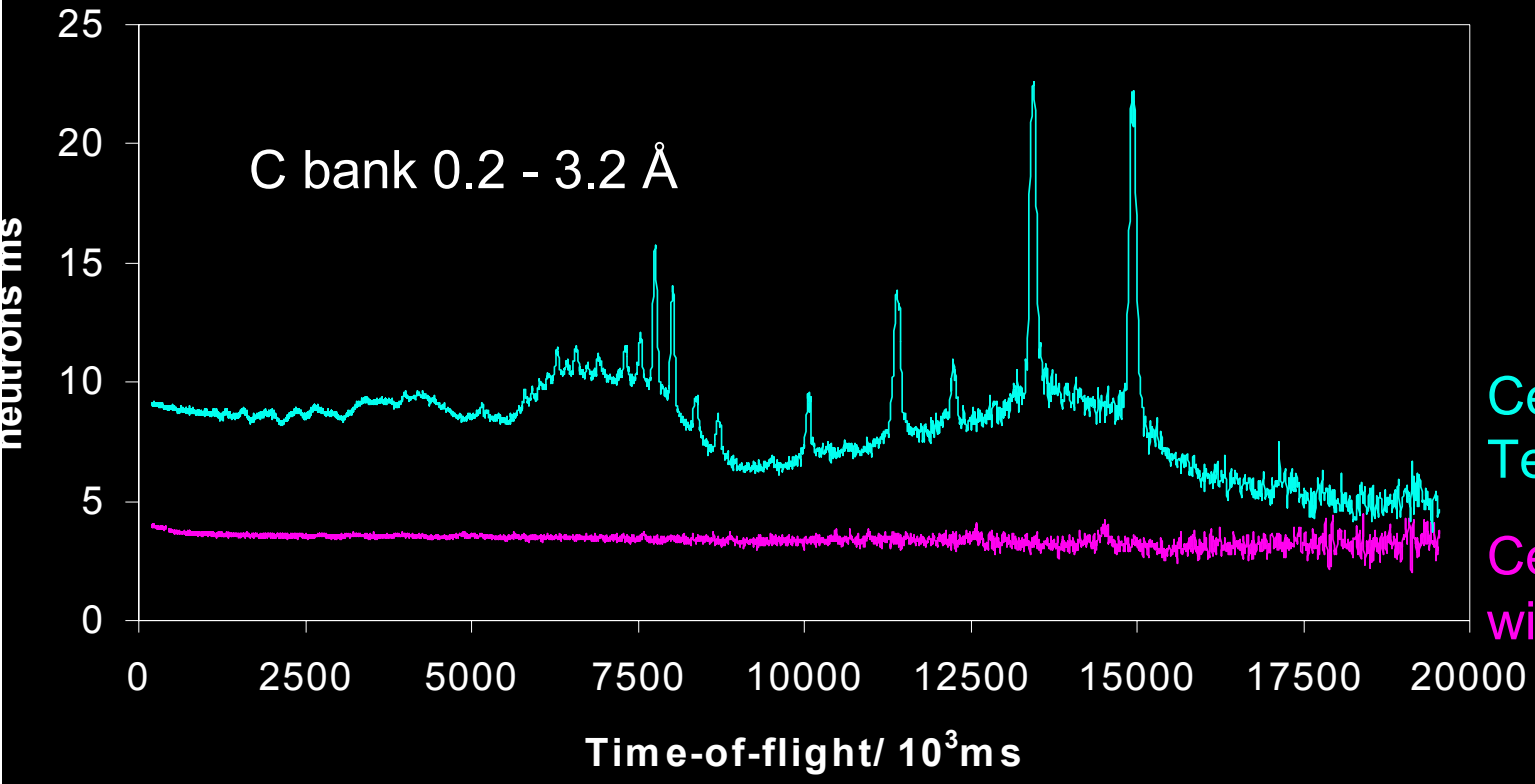
DETECTORS:	4200 ↑ 6600 "Conventional" 7-bank structure (resolution-focused).
SOLID ANGLE:	2.85 ↑ 4.2 Sterad.
CHOPPERS:	3 choppers (λ-selector, frame overlap, nimonic).
Q-RANGE:	Very high Q_{MAX} ($E \leq 1$ eV, $\lambda \geq 0.28$ Å).
RESOLUTION:	~0.2% in back-scattering.
DATA SET SIZE:	64 Mbytes ↑ 128 Mbytes
DATA RATE (PEAK):	6 Gbytes-500 files/day
DATA RATE (AVE):	1 Gbyte-40 files/day

Schematic Diagram of the Detector Array on the New GEM Diffractometer at the Isis Facility




22/2/2008

Hydrothermal Cell Background



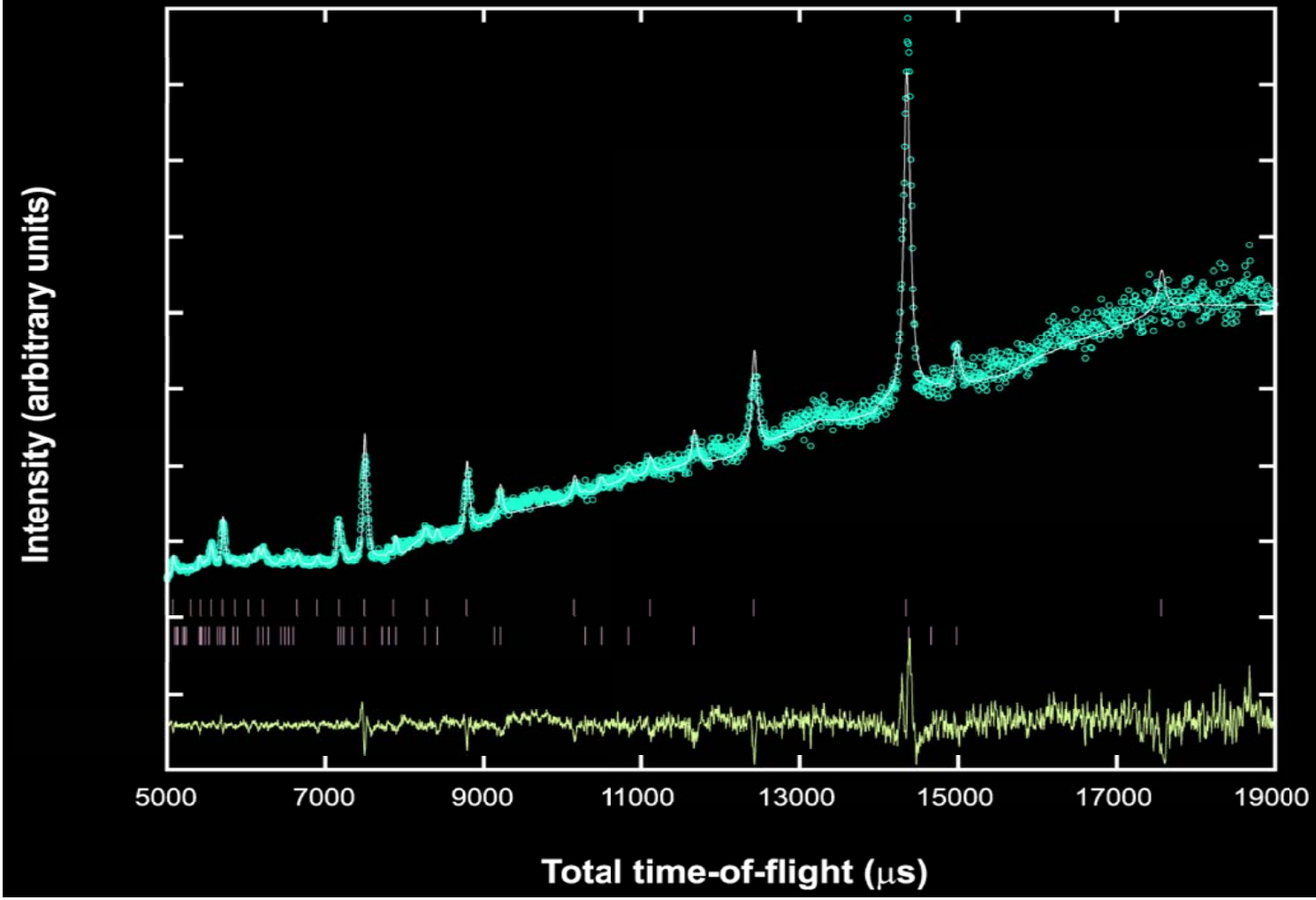
Cell with a 0.5 mm Teflon™ Liner

Cell internally sputtered with 100 μm of gold

The cell gives rise to virtually no background and provides a chemically inert environment.

Rietveld Refinement of the TOF Neutron Powder Diffraction Data for $BaTiO_3$

In the Hydrothermal Cell at 120 °C



Refined Parameters

- Background, peak profile
- Unit cell parameters of $BaTiO_3$ and TiO_2

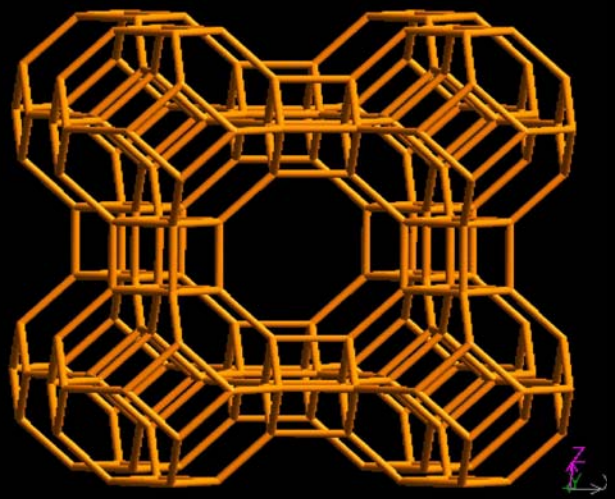
Time-Resolved *In-Situ* Powder Neutron Diffraction

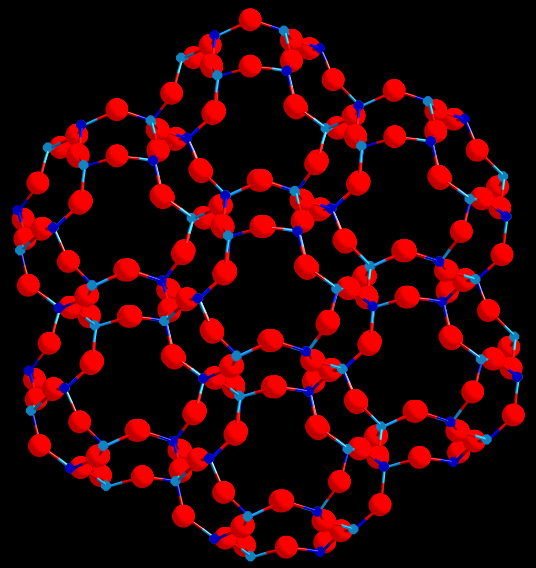
- **Hydrothermal Chemistry**
  - Synthesis of Zeolites
  - Synthesis of *t*-$BaTiO_3$

Hydrothermal Synthesis of Sodalite

Synthesis:

$$2\ SiO_2 : 1\ Al_2O_3 : 4\ Na_2O : 17\ D_2O \xrightarrow{100\ °C} Na_8[Al_6Si_6O_{24}](OD)_2.2D_2O$$





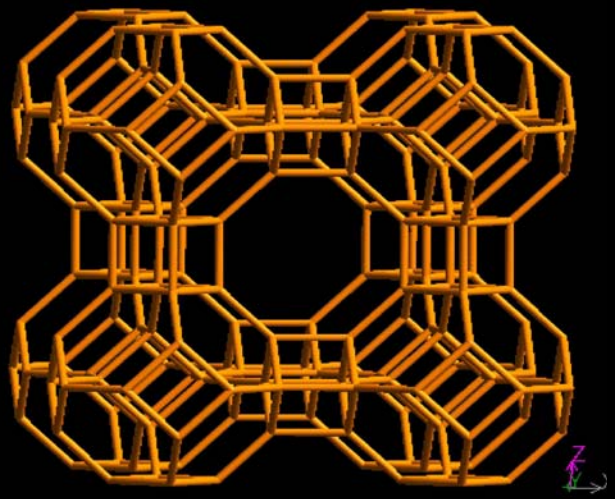
- Apertures formed by 6-rings only
- Cubic, $P\bar{4}3n$
- *a* = 8.9 Å

Crystallisation of Zeolite A and Hydroxosodalite

$Al_2O_3 : 2SiO_2 : n\ NaOH : x\ H_2O$

Low NaOH concentration

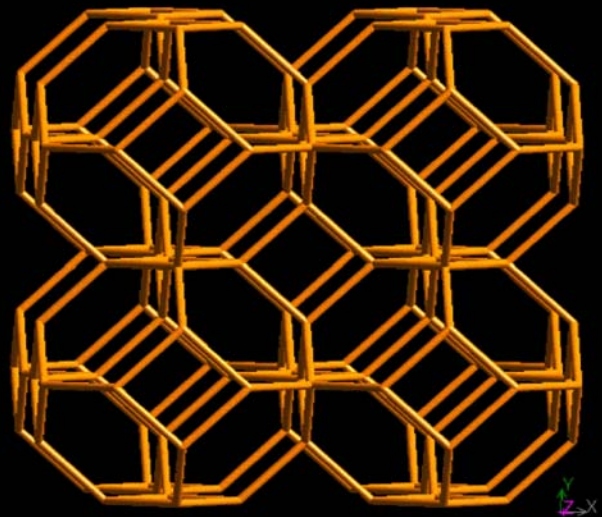
High NaOH concentration



Sodium zeolite A (LTA)

$Na_{12}[Si_{12}Al_{12}O_{48}].27H_2O$

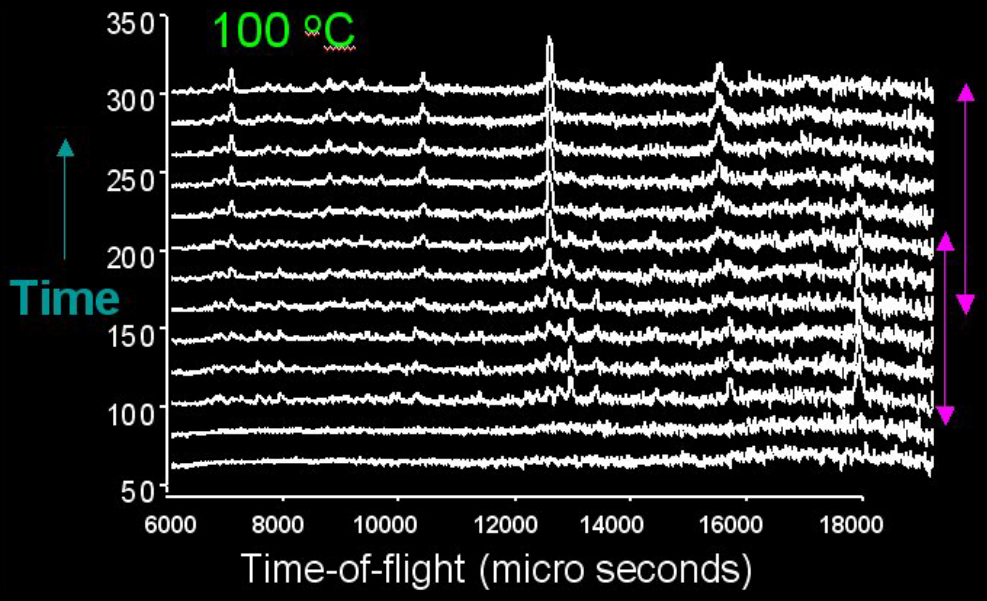
Long reaction times



Hydroxosodalite (SOD)

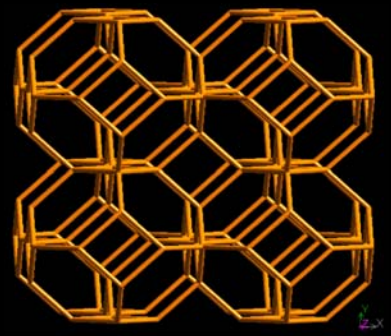
$Na_8[Si_6Al_6O_{24}](OH)_2.2H_2O$

Time-Resolved Powder Neutron Diffraction Data for the Hydrothermal Transformation of Zeolite A to Hydroxosodalite

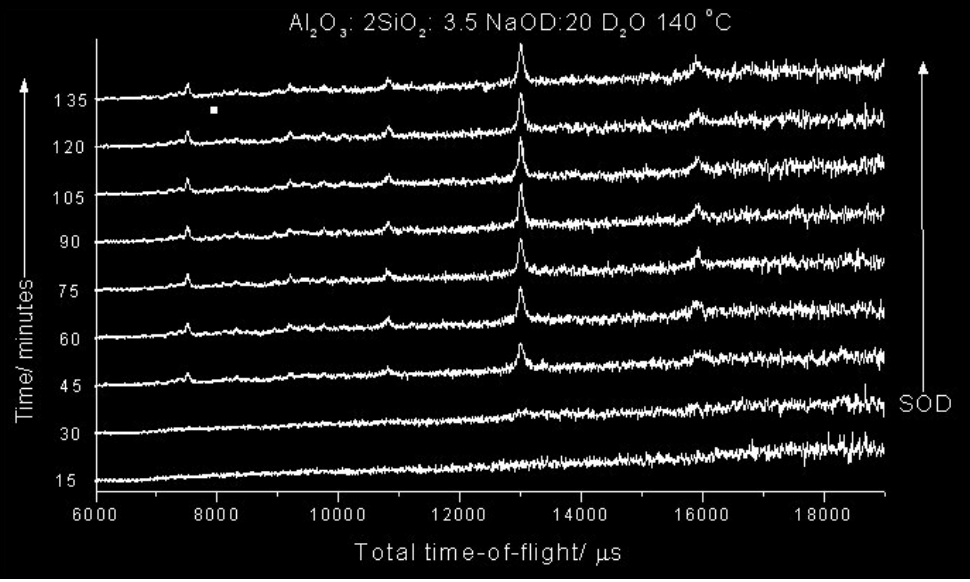


direct crystallisation of sodalite

at higher pH:
collapses into the denser sodalite phase

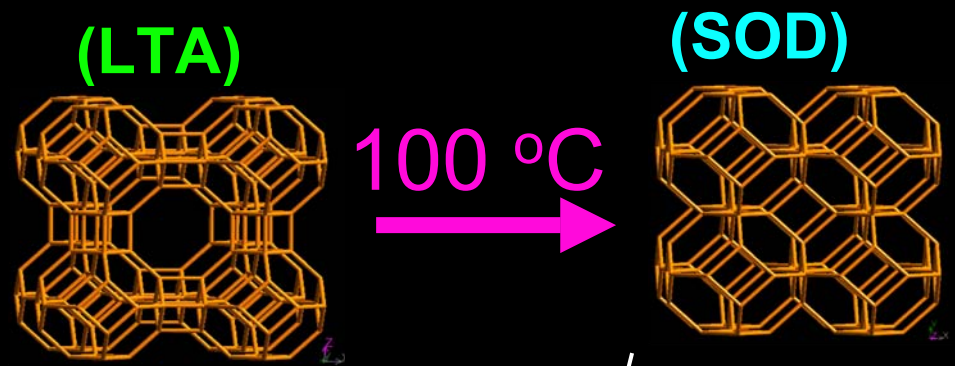


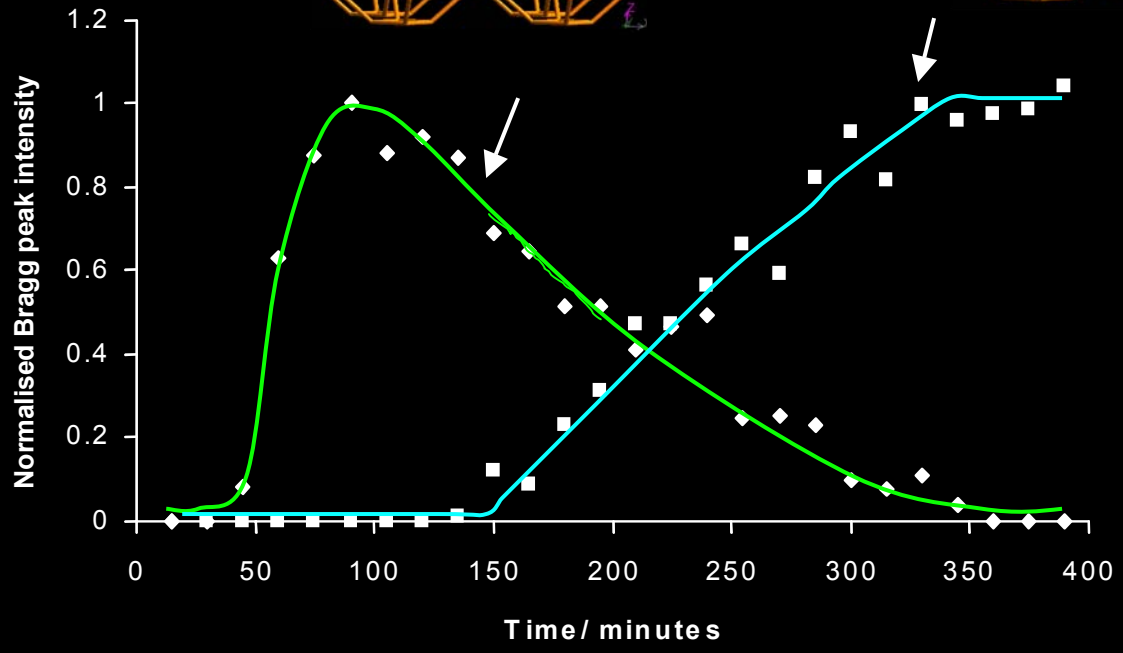
140 °C:



Growth Kinetics Obtained from *in situ* Powder Neutron Diffraction Data

$Al_2O_3 : 2SiO_2$:
3.5 NaOD: 20 D_2O

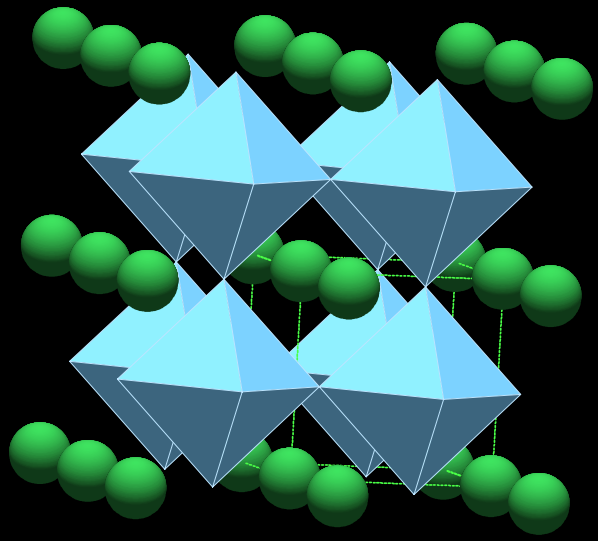




- Follows Ostwald's rule of successive crystallisations

Hydrothermal Synthesis of $BaTiO_3$

TiO_2 + { $Ba(OH)_2.8H_2O$ or $BaCl_2$ + NaOH } $\xrightarrow[120\text{ -}200\ ^\circ C]{H_2O}$



t-$BaTiO_3$

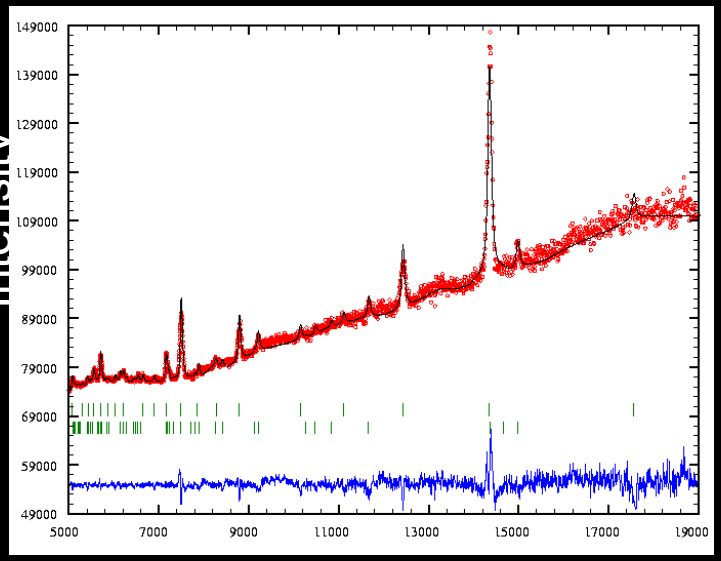
Hydrothermal method provides;

- slow temperature synthesis
- small (submicron) particle size
- good particle size distribution

- **Ferroelectric material**
- **High permittivity**
- **Applications**
  DRAM, electro-optic devices, capacitors

Following the Hydrothermal Crystallisation of $BaTiO_3$ using *in-situ* Powder Neutron Diffraction

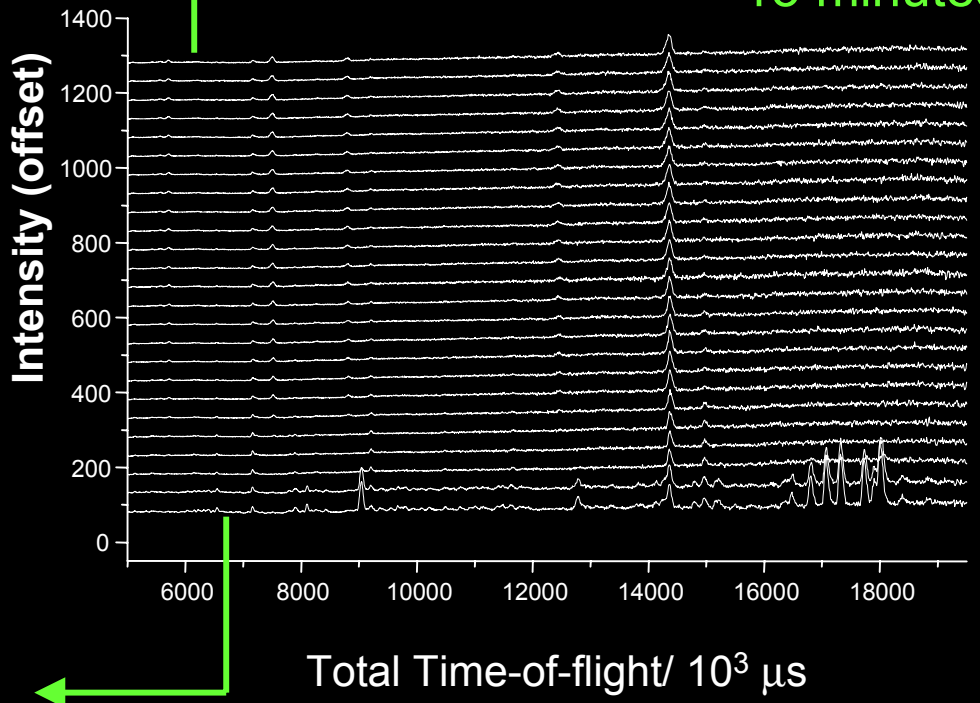
POLARIS Diffractomete

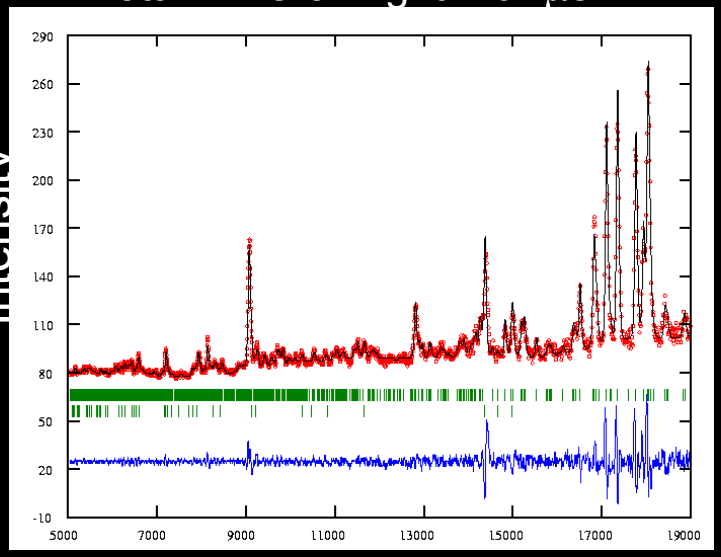


12 hours: $BaTiO_3$

125 °C

15 minutes per spectrum

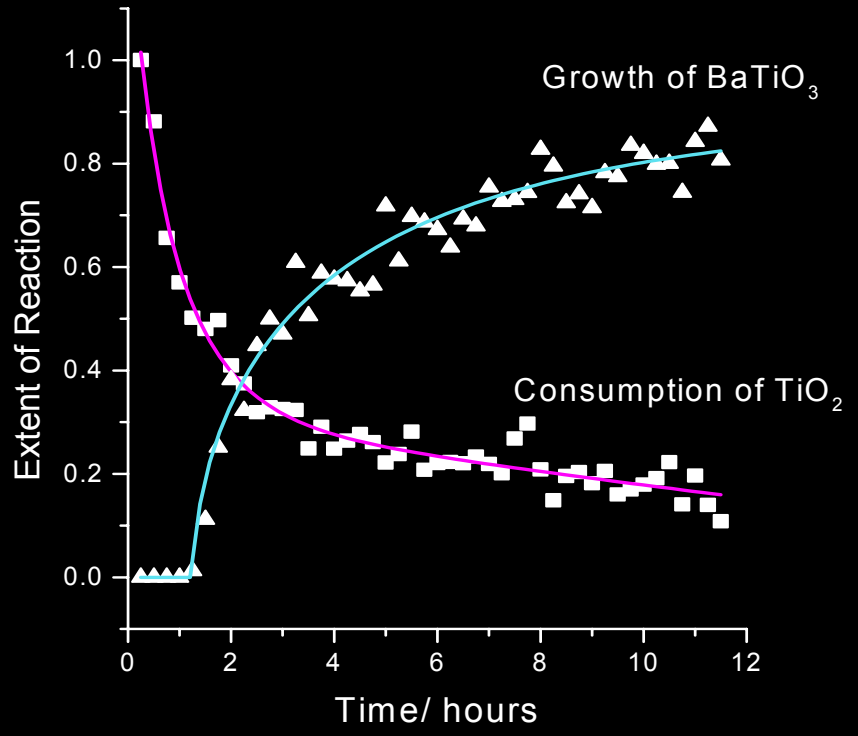


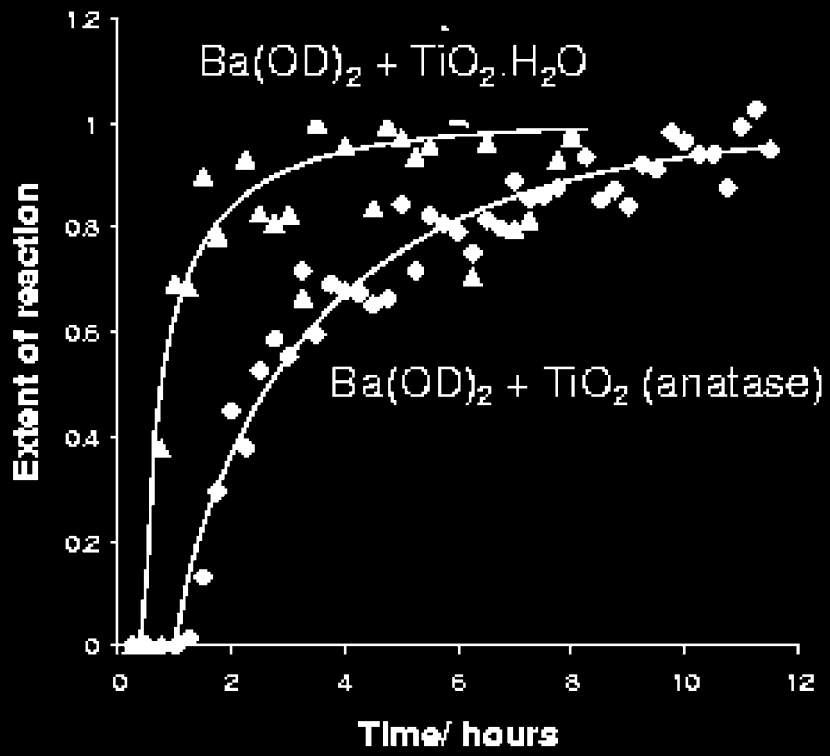


15 minutes: $Ba(OD)_2.8D_2O + TiO_2$

Walton *et al.* Chem. Commun. (2000) 1267

Growth Kinetics of $BaTiO_3$ from *in-situ* Powder Neutron Diffraction





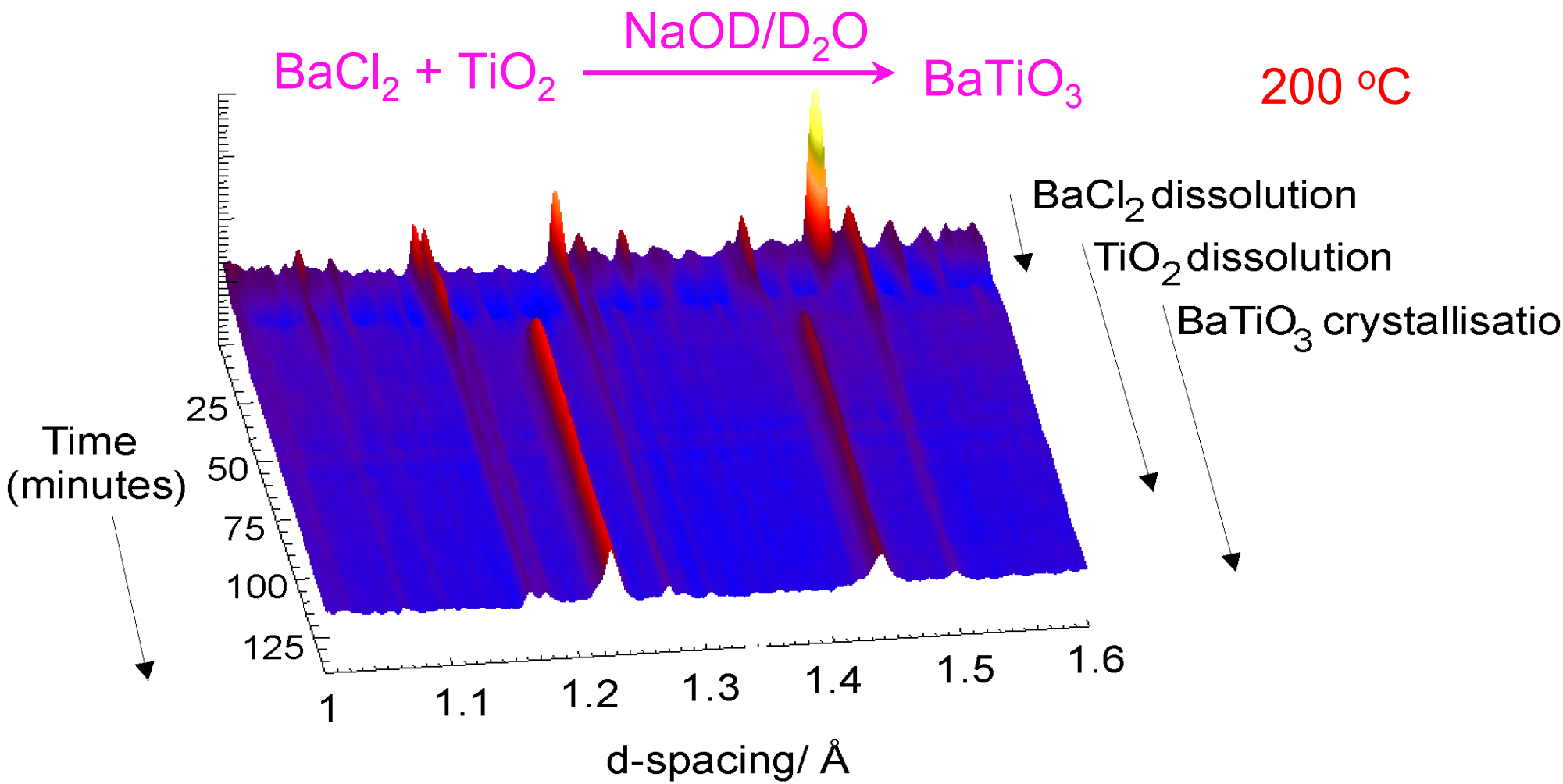
First *in situ* study of the hydrothermal crystallisation of $BaTiO_3$

- Large amount of TiO_2 dissolves before $BaTiO_3$ is observed
- Small particle-size amorphous Ti source - markedly faster crystallisation

$\Rightarrow$ dissolution-precipitation mechanism

- Suggests a reaction between solution phase $Ti(OH)_x^{4-x}$ and Ba^{2+} ions

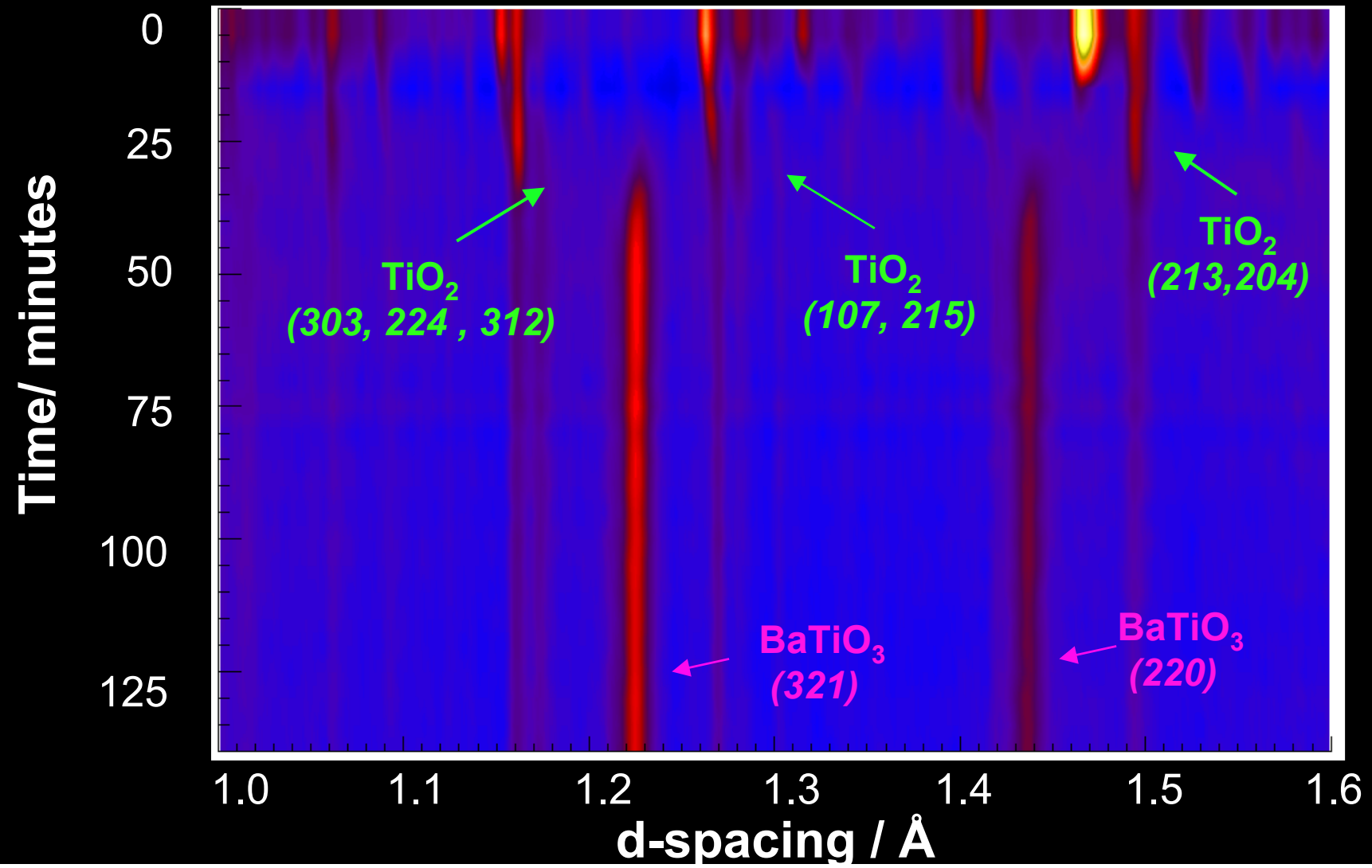
Crystallisation at Barium Titanate



Each of the tof neutron data sets was measured in 5 minutes on GEM

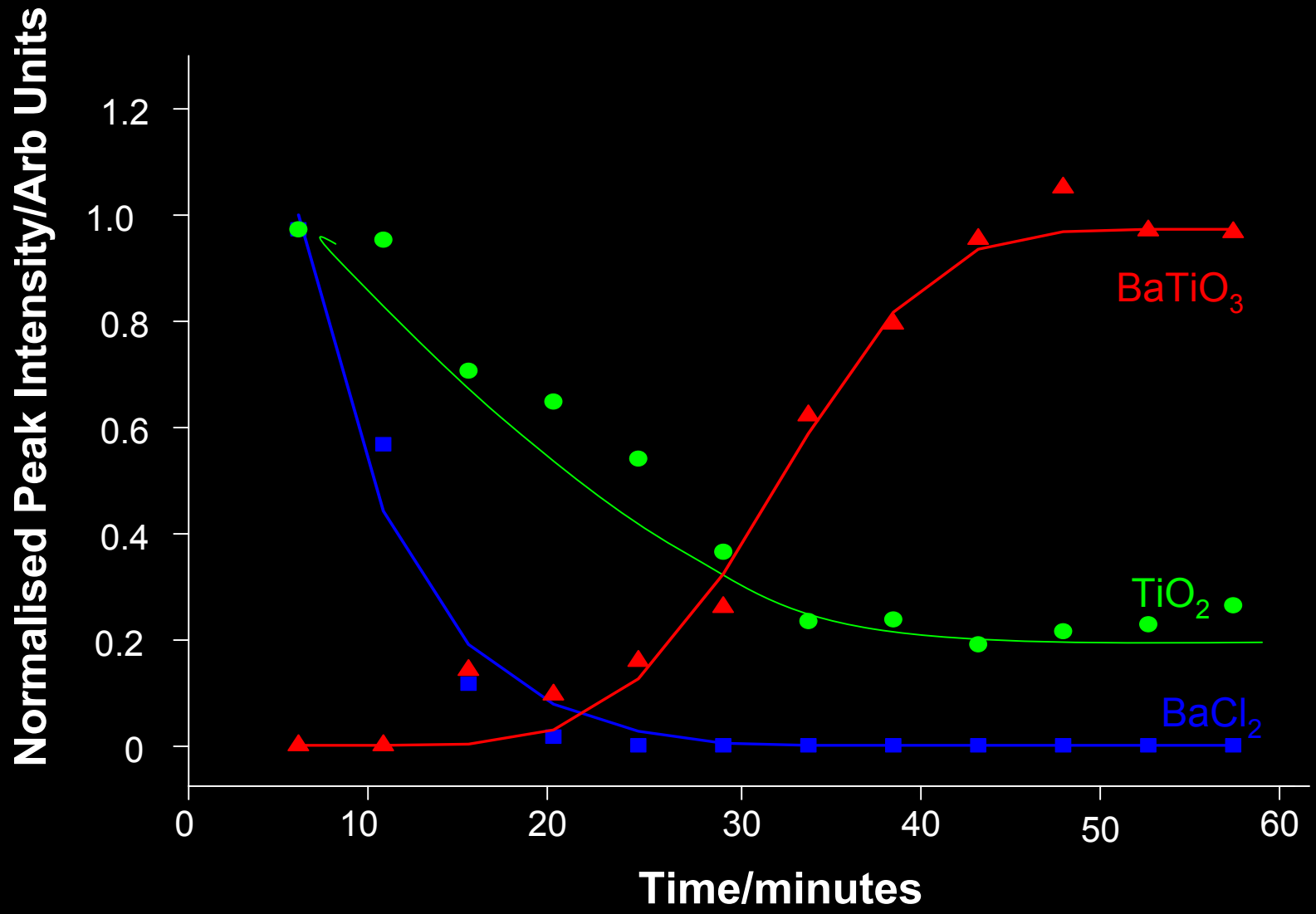
Time-Resolved in-situ Powder Neutron Diffraction Data for the Hydrothermal Crystallisation of $BaTiO_3$

Synthesis Conditions: 1.1$BaCl_2$: TiO_2: 3.33 NaOD: 16.7 D_2O at 200 ^oC



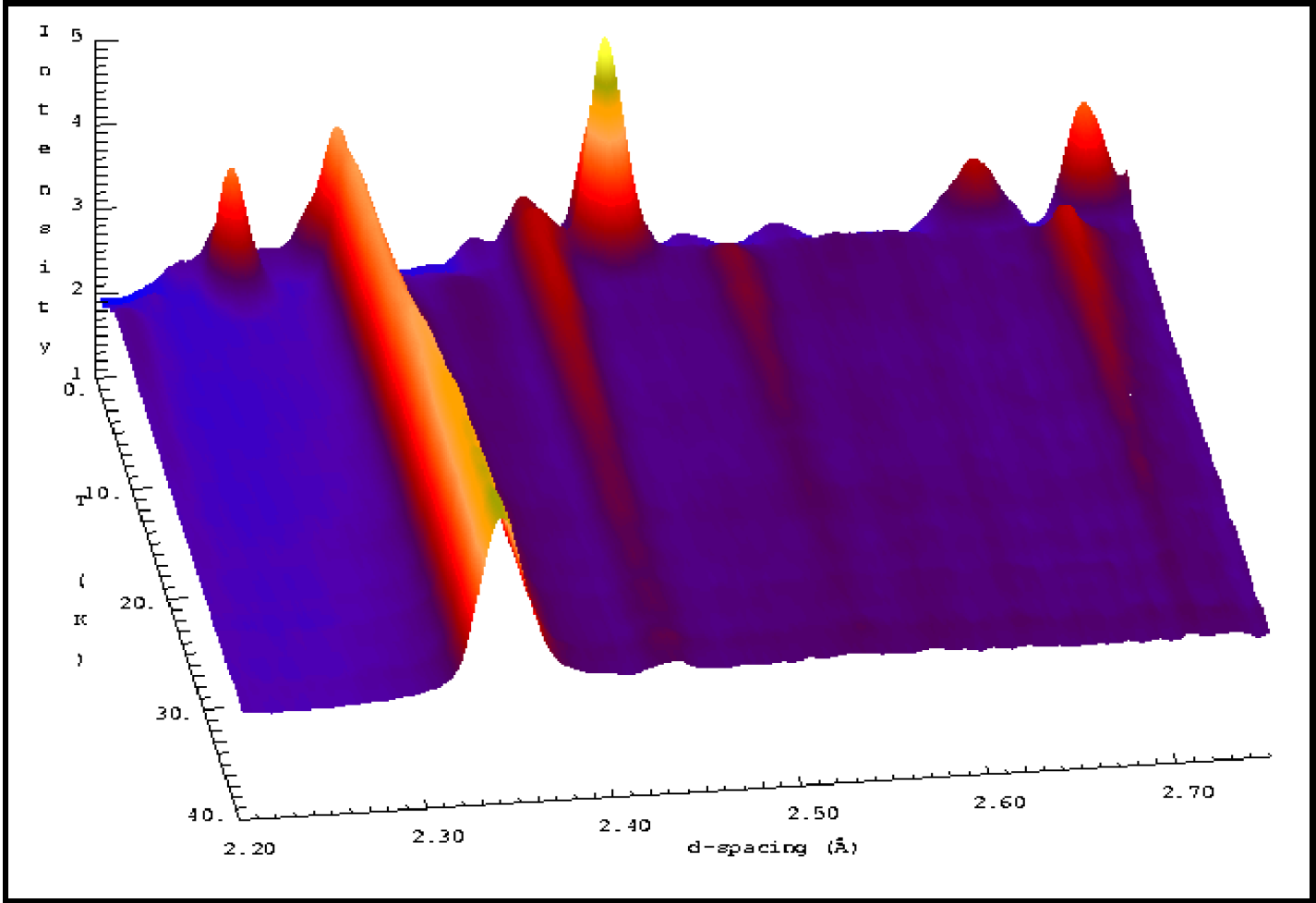
Normalised Integrated Bragg Peak

Synthesis Conditions: 1.1$BaCl_2$: TiO_2: 3.33 NaOD: 16.7 D_2O at 200 ^oC



Crystallisation of Barium Titanate

$$BaCl_2 + TiO_2 \xrightarrow{NaOD/D_2O} BaTiO_3$$

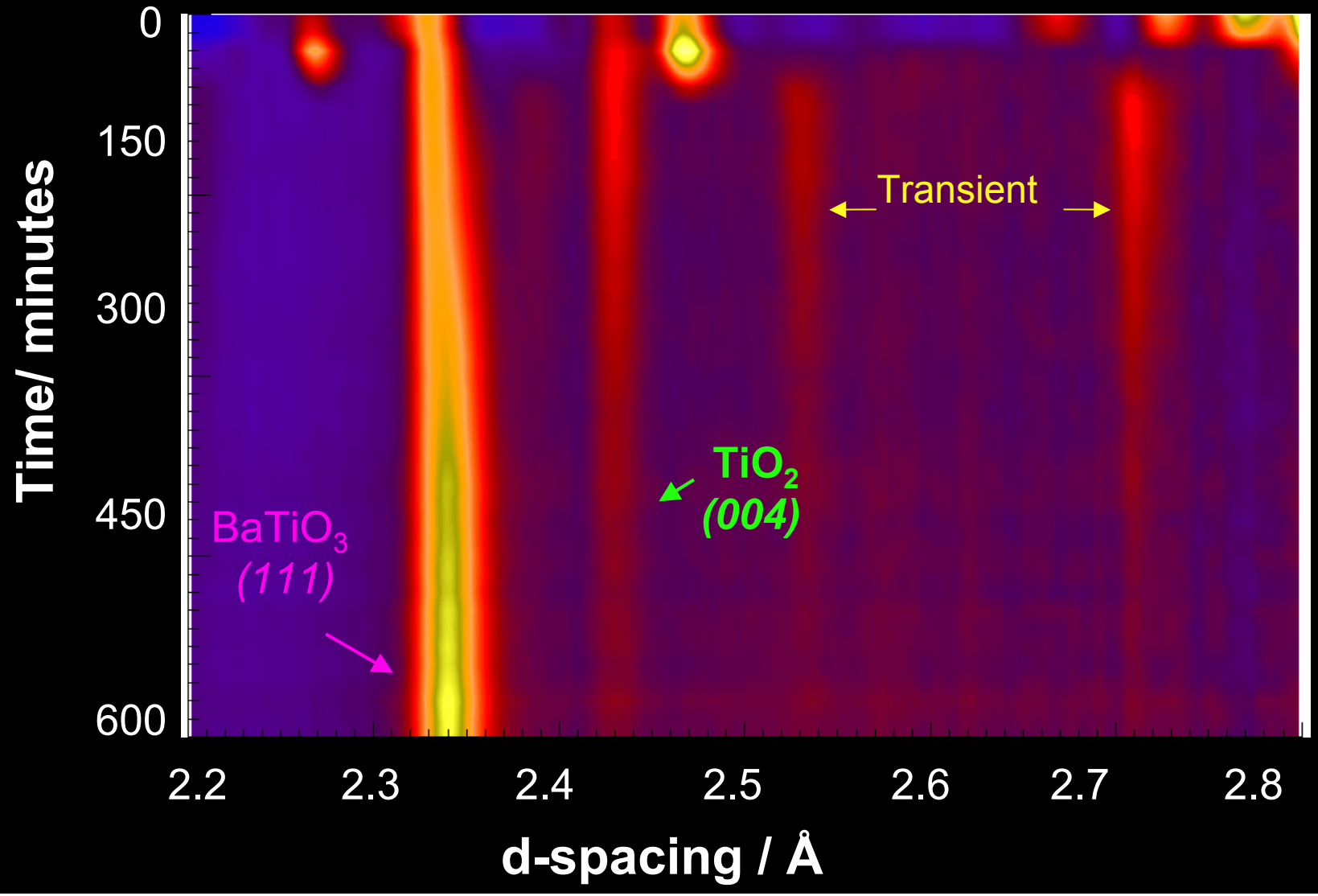


125 °C

- Competitive formation o a second phase
- Identified as Ba_2TiO_4

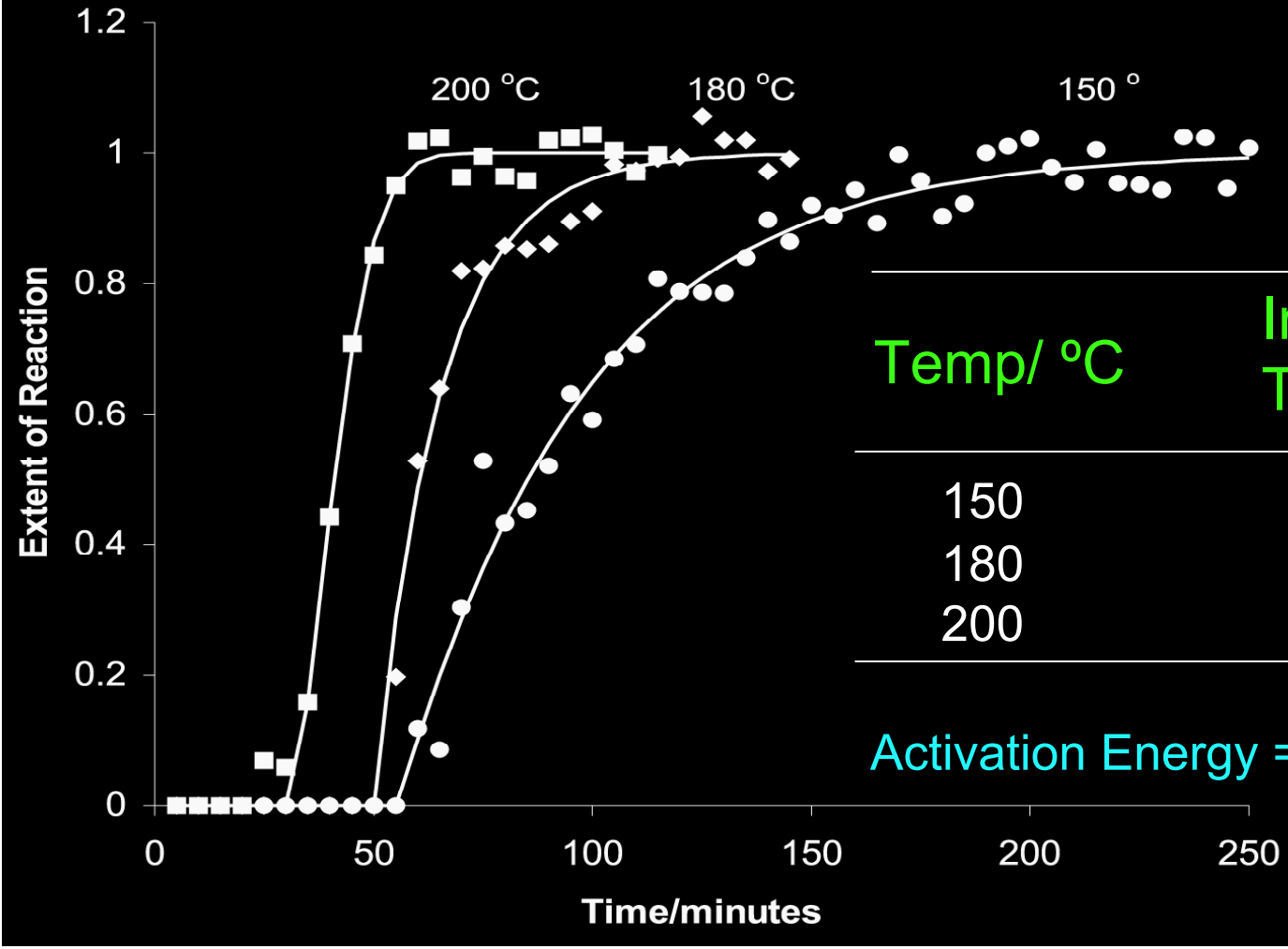
Time-Resolved in-situ Powder Neutron Diffraction Data for the Hydrothermal Crystallisation of $BaTiO_3$

Synthesis Conditions: 1.1$BaCl_2$: TiO_2: 3.33 NaOD: 16.7 D_2O at 125 ^oC



Rate of Crystallisation of $BaTiO_3$

Effect of temperature

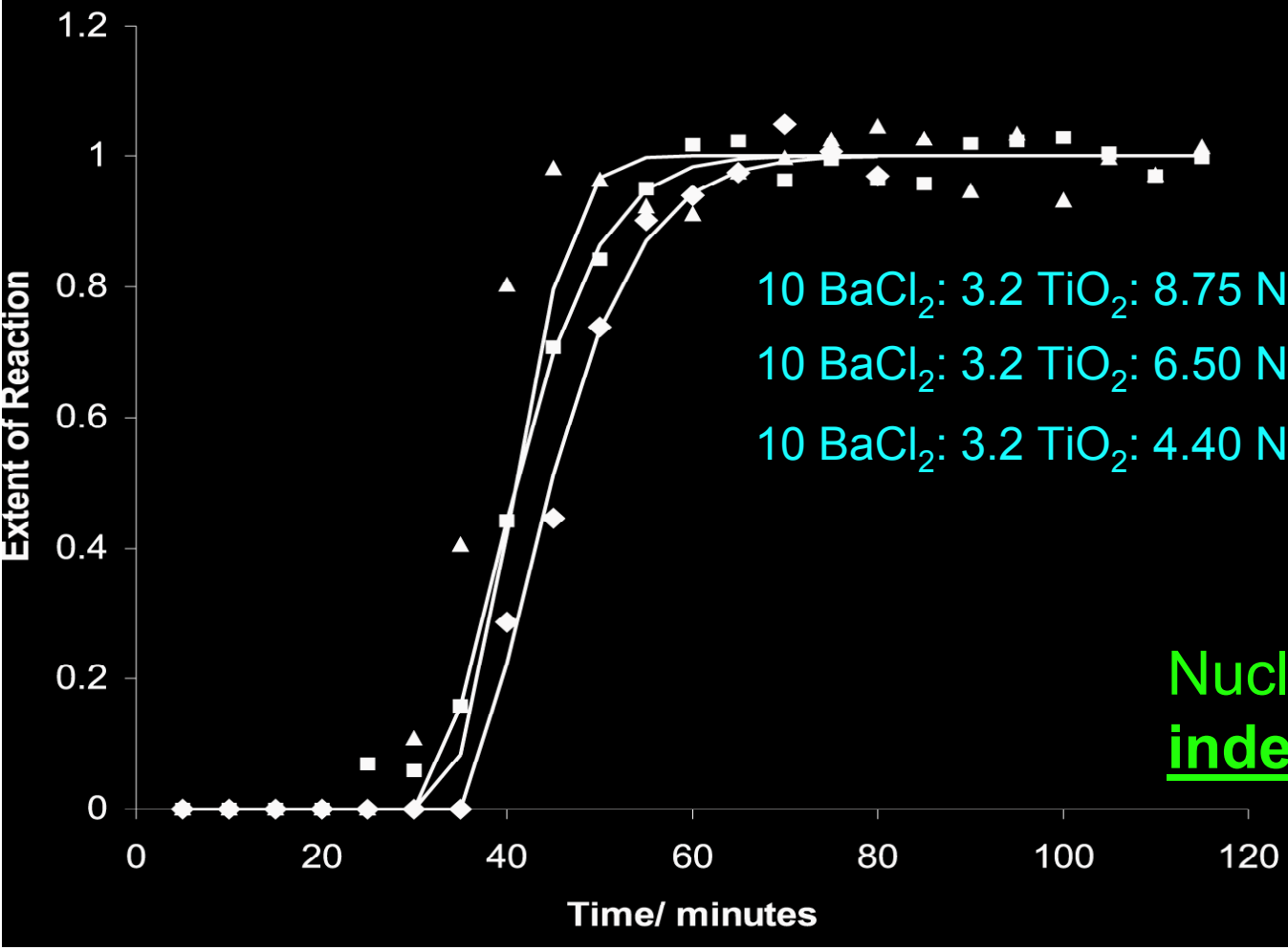


Temp/ °C	Induction Time/ min	Rate/ min^{-1}
150	35	0.122
180	50	0.066
200	55	0.023

Activation Energy = 55.1 kJ Mol^{-1}

Rate of Crystallisation of $BaTiO_3$

Effect of NaOD Concentration



10 $BaCl_2$: 3.2 TiO_2: 8.75 NaOD: 13.8 D_2O

10 $BaCl_2$: 3.2 TiO_2: 6.50 NaOD: 16.0 D_2O

10 $BaCl_2$: 3.2 TiO_2: 4.40 NaOD: 18.2 D_2O

Nucleation and growth is **independent** of pH

Conclusions from this Study of the Hydrothemal Synthesis of *t*-$BaTiO_3$

- $BaTiO_3$ begins to crystallise at *ca*. 20 mins and is complete at *ca*. 40 mins.
- Both $Ba(OH)_2$ and $BaCl_2$ starting materials dissolve before the onset of crystallisation.
- A significant amount of TiO_2 dissolves immediately on heating, and before the onset of $BaTiO_3$ crystallisation.
- At 125 ºC a transient crystalline intermediate (Ba_2TiO_4) is observed.
- The nucleation time and growth rate is independent of pH.

Conclusions

In situ diffraction methods provide an efficient means of following hydrothermal reactions under *real conditions*

Energy-Dispersive X-ray Powder Diffraction

- high time resolution (< 1 minute)
- kinetic data of unrivalled quality
- modelling kinetic data gives mechanistic information
- transient crystalline phases can be observed

Powder Neutron Diffraction

- diffraction data have high resolution
- structural information from *in situ* diffraction data
- higher neutron fluxes and the use of position-sensitive detector banks will vastly improve data acquisition rates

Acknowledgements

Time-Resolved Experiments

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